ELECTRON SPIN RESONANCE INVESTIGATION OF THE EFFECTS OF THE H2+ IMPLANTATION AND DIFFUSION ONE THE LASER INDUCED DEFECTS IN VIRGIN SILICON

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ELECTRON SPIN RESONANCE INVESTIGATION OF THE EFFECTS OF THE H_2^+ IMPLANTATION AND DIFFUSION ONE THE LASER INDUCED DEFECTS IN VIRGIN SILICON

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Résumé - La résonance paramagnétique électronique des défauts produits par le recuit laser, à des densités de puissance élevées (2 J/cm^{-2}) a été étudiée dans le silicium semi-isolant non dopé, obtenu par croissance en zone flottante. Aucun effet n'est observé sur la raie à g_X = 2,0055 ± 0,0005, après implantation de H_2^+, après diffusion de l'hydrogène. Ceci est en accord avec l'attribution de X à des liaisons pendantes créées par des contraintes mécaniques pendant le choc thermique. En effet, on sait que ces défauts ne sont pas passivés par l'hydrogène moléculaire.

Abstract - Electron paramagnetic resonance of the defects induced by laser annealing at high power density (2 J/cm^{-2}) has been investigated in virgin FZ semi-insulating Silicon. A further H_2^+ implantation and diffusion is inactive on the signal observed at g_X = 2.0055 ± 0.0005. This is consistent with the attribution of X to the dangling bonds, created by the mechanical stresses during the thermal shock, as they are not passivated by molecular hydrogen.

INTRODUCTION

Laser anneal at higher energy (more than 1.6 J/cm^{-2} for ruby laser) creates defects in virgin Si.

These have been evidenced as well by electrical measurements as by electron paramagnetic resonance (EPR) /1/.

Electron paramagnetic resonance (EPR) experiments have shown that an unidentified defect X, characterized by an isotropic LANDE factor g = 2.0055 ± 0.0005 was associated with high intensity pulsed laser irradiation of virgin silicon wafer material. Chemical etching showed that its creation was indeed limited to surface layer of about 1 µm thickness; further, this center disappears again upon a thermal anneal at 500° C /1 -4/.

Tentatively this signal was ascribed to two possible models, either the vacancy-oxygen complex (V-O_i) or the trivalent Si^{3+} (or dangling bond), the actual isotropic value of the g factor resulting from an orientational averaging in both cases. For each model, the EPR signal intensity corresponds to some 10^{13} centers per cm^2 of irradiated surface; taking into account that the defects are within a surface layer of about 1 µm thickness, this corresponds to a local concentration of some 10^{17} cm^{-3}.

On the other hand, electrical transport measurements like DLTS /1/ have confirmed that two energy levels at E_c - 0.18 eV (E_1) and E_v + 0.33 eV (H_1) can be correlated to oxygen related defects, which are also disappearing after a thermal anneal at 500° C.

Some of the defects observed in Si become inactive, as well electronically as for their EPR signature, when hydrogen is added. This occurs for the dangling bonds in amorphous or polycrystalline Silicon, which are no more observed after doping with atomic hydrogen; however, molecular hydrogen is not efficient /5, 7/.

H_2^+ implantation has been used more recently to cure detrimental effects on devices due to surface recombination centers.

In this context, we have performed a comparative study of laser generated defects, prior and after H_2^+ passivation using EPR as an investigation tool. It is shown that the main X defect at g_x = 2.0055 is not affected by this treatment; this is still consistent with the attribution of g_x to the dangling bond model.

EXPERIMENTAL

The starting material was high purity floating zone Si of 10^4 Ωcm resistivity, cut into 1 x 3 x 6 mm^3 and chemically etched by CP 4 before laser treatments.

Anneals were performed in air by means of a pulsed ruby laser with pulse duration of 20 ns. The energy density on the samples was set at 2 J/cm^{-2} and ten successive shots were applied on both main sides.

Molecular hydrogen H_2^+ at 10^{17} cm^{-2} density was implanted at very low incident energy (2 KeV). Since the X center are concentrated in a 1 μm top layer, this step had to be followed by a diffusion procedure to insure a sufficient penetration depth of the H_2^+ species. In order to avaid a thermal anneal of the X center, stable until 500° C, diffusion was performed at 180° C, a temperature which is at least 100° C below any thermal recovery temperature of defects of similar EPR signature C'. Duration was 10 mn insuring a penetration depth of 5-8 μm according to Ref. 8.

X band EPR measurements were performed at 4.2 K using a stack of three samples to increase sensitivity. Checking experiments were performed on blank reference samples, after H_2^+ implantation and finally after diffusion. The spectra have been recorded after cooling down in the dark, then with a band to band photoexcitation (λ ∿ 1 μ), to assess light induced effects.

RESULTS

The virgin silicon samples are nearly EPR-free, even at 4.2 K (Fig. 1).

This is no longer the case after the laser treatment (Fig. 2) : an isotropic line X appears with an isotropic LANDE factor g_x = 2.0055 ± 0.0005. The peak to peak field difference on the experimental absorption derivative is (12 ± 1) G. The intensity corresponds to 10^{13} - 10^{14} per cm^2 of the irradiated surface.

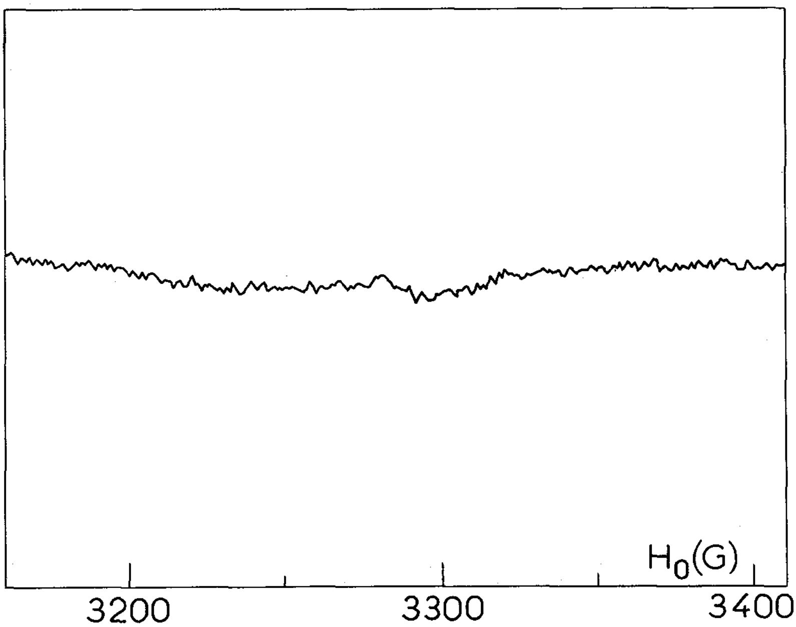

Fig. 1 - EPR spectrum of virgin Si at 4.2 K

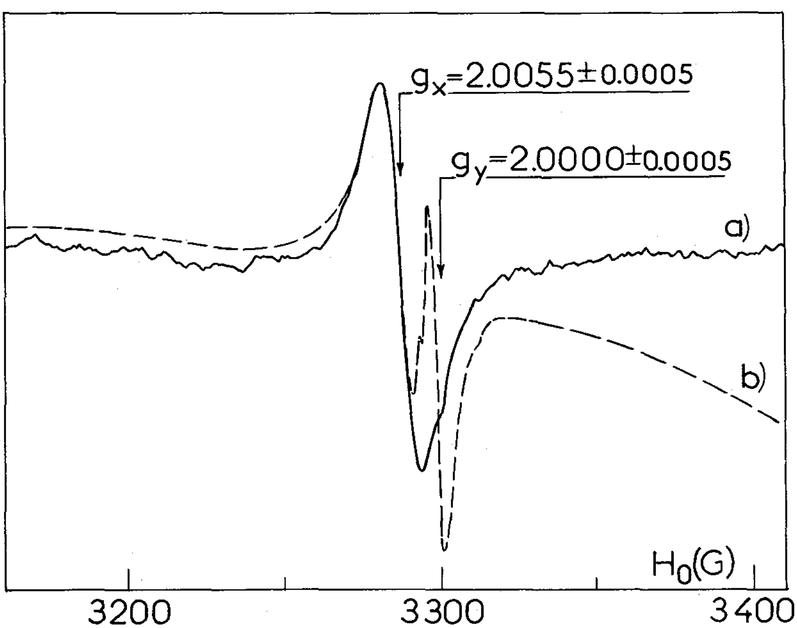

Fig. 2 - EPR spectrum of Si after laser anneal at 4.2 K
a) after cooling down in the dark
b) during photoexcitation (λ = 1 μ)

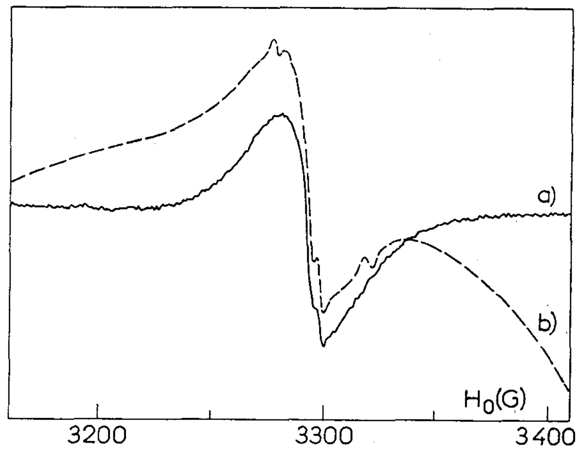

Fig. 3 - EPR Spectrum of Si after laser anneal and H_2^+ implantation, at 4.2 K.
a) after cooling down in the dark
b) during photoexcitation (λ = 1μ)

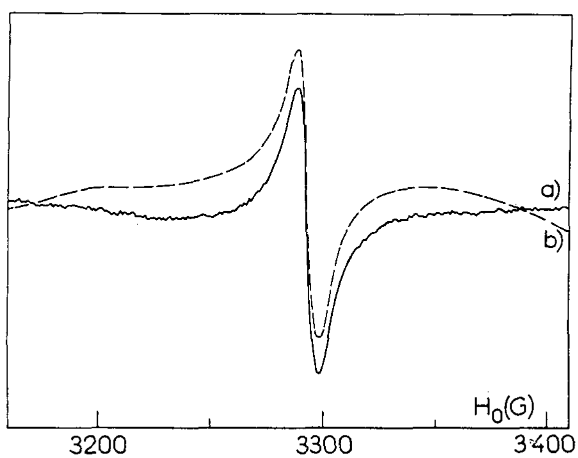

Fig. 4 - EPR Spectrum at 4.2 K of Si after laser anneal H_2^+ implantation, and 10 min at 180° C :

a) after cooling down in the dark
b) during photoexcitation (λ = 1 μ)

After H_2^+ implantation (Fig. 3), the linewidth of the absorption line broadens and and the centroïd is displaced slightly toward lower fields. After a thermal anneal at 180° C to induce a diffusion of hydrogen (Fig. 4), the resonance line becomes narrower, the signal X has again the same shape and intensity as before H_2^+ implantation.

During photoexcitation X is not affected, whereas a narrow and weaker isotropic signature Y is observed after laser annealing at $g_x = 2.0000 \pm 0.0005$; it vanishes after H_2^+ implantation.

DISCUSSION

In these experiments, we observe in a reproducible way, the signal at $g_x = 2.0055 \pm 0.0005$, correlated to high power density laser annealing.

This signal does not vanish after our subsequent hydrogen doping treatments, neither after H_2^+ implantation nor after a thermal treatment at 180° C. This is still consistent with one of our previous models for X, the trivalent Si dangling bond, as the latter is not affected by the molecular but only by the atomic hydrogen diffusion.

It has been shown recently that the dangling bond acts as a carrier pair recombination center at $E_v + 0.4$ eV /9/; This is also consistent with the simultaneous electron and hole lifetime decrease determined in virgin Si previously /3/.

The creation of these defects, which are distributed well behind the melted layer, can therefore not be ascribed to a fast contaminant redistribution. We ascribe it the extended defects induced by the mechanical stresses during the thermal shock leaving then dangling bonds in these locally disordered areas.

Finally, in this Si sample, we were able to evidence a further weak shallow donor line. Its behaviour can give a hint for the processes related to the resistivity changes which are sometimes observed after laser treatments. We observe that the contaminant responsible for the donor signal is only active after the laser shot : a similar behaviour was observed previously by EPR after P doping /2/. After H_2^+ implantation, Y vanishes : these defects are then compensated by implantation defects whose EPR is responsible of the apparent broadening of X. Where then defects are annealed, at 180° C, the true shape of X is restored.

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